
17 Electroanalytical Techniques and Instrumentation in Food Analysis

Rubin Gulaboski and Carlos M. Pereira

CONTENTS

17.1	Introduction.....	379
17.2	Principles of Voltammetric Techniques.....	380
17.3	Theory and Definitions in Voltammetric Techniques	381
17.4	Instrumentation in Voltammetric Experiments.....	382
17.4.1	Potentiostat	382
17.4.2	Electrochemical Cell and Electrodes.....	383
17.5	Short Review of Some Common Voltammetric Techniques Used in Food Analysis	384
17.5.1	Cyclic Voltammetry	384
17.5.2	Pulse Voltammetric Techniques.....	386
17.5.2.1	Normal Pulse Voltammetry.....	386
17.5.2.2	Differential Pulse Voltammetry.....	387
17.5.2.3	Square-Wave Voltammetry	388
17.6	Preconcentration Voltammetric Techniques	389
17.6.1	Adsorptive Stripping Voltammetry.....	389
17.6.2	Anodic Stripping Voltammetry.....	389
17.6.3	Cathodic Stripping Voltammetry	390
17.7	Electrochemical Techniques in Food Analysis.....	390
17.7.1	Food Colorants.....	390
17.7.2	Metal Contaminants	390
17.7.3	Pesticides and Herbicides.....	391
17.7.4	Biosensors	395
17.7.5	Other Applications	395
17.7.6	Hyphenated Techniques	395
17.8	New Trends.....	396
	References	396

17.1 INTRODUCTION

Electrochemical techniques are inevitable tools in almost every chemical and biochemical research laboratory. In addition to their application in fundamental studies of oxidation and reduction processes to unravel reaction mechanisms, these techniques are also used in studying the kinetics and thermodynamics of electron and ion transfer processes [1]. Moreover, electrochemical techniques have also proven to be useful tools for the study of adsorption and crystallization phenomena at electrode surfaces [2]. Among the electrochemical techniques applied in food analysis, the

principal ones are polarographic and voltammetric techniques [3]. Their wide application is attributed with the relatively cheap instrumentation, very good sensitivity with wide linear concentration ranges for both inorganic and organic compounds, rapid analysis times (in seconds), and simultaneous determination of several analytes. Currently, polarographic techniques have almost been completely excluded from research laboratories, and are being replaced by the more sophisticated voltammetric techniques [1]. Voltammetry (abbreviation of volt-ampere-metry) is a branch of electrochemistry that was developed by the discovery of polarography in 1922 by Jaroslav Heyrovsky (Nobel Prize in 1959). A major breakthrough in voltammetry was made in the early 1960s, when an expanded repertoire of analytical methods were reported, appearing in parallel with the corresponding well-developed theories [1,4]. At the same time, these developments led to enhanced sensitivities obtained with the voltammetric techniques. The excitation signal in all voltammetric techniques is the applied potential difference (or potential as it is commonly referred to), E , between the electrodes, whereas the monitoring output parameter is the resulting current, I , flowing through the electrochemical cell.

Electrochemistry provides powerful and versatile tools for food analysis: powerful with regard to detecting very low concentrations, while providing a wide linear relationship between the measured signal (current intensity) and concentration; versatile as a consequence of the possibility of simultaneous analysis, extended to a large number of organic and inorganic compounds that can be found in food. One of the main advantages of electrochemical techniques is usually considered to be the possibility of direct analysis of the sample without tedious and long preparative steps and subsequent separation. Voltammetric measurements can be applied directly to colored systems, in the presence of suspended matter, or even to colloidal systems. When using biological or complex environmental samples, pretreatment is required. However, this process is faster, cheaper, and easier when compared with the standard treatment used to prepare samples to be analyzed by chromatographic techniques [5]. When compared with chromatographic techniques, effect of interference found is low when electrochemical techniques are used [6]. If required, voltammetric methods can also easily be hyphenated with other techniques, e.g., their use as detectors in chromatographic separations [7]. Another advantage of voltammetric techniques in food analysis is the various possible modes and methodologies that can be used for the determination of both electrochemically active and electrochemically inactive compounds [8].

17.2 PRINCIPLES OF VOLTAMMETRIC TECHNIQUES

Voltammetric experiments are usually carried out in simple electrochemical cells, similar to that shown in Figure 17.1. A common electrochemical cell consists of a working electrode, a reference electrode, and usually an auxiliary (counter) electrode. The working electrode is an electron conductor at which the reaction or transfer of interest takes place. In all voltammetric experiments, it is necessary to keep one of the electrodes at a constant potential. This electrode, designed to have a constant (reversible) potential, is called a reference electrode. The auxiliary electrode is one at which a counter reaction to that at the working electrode takes place, for the sake of balancing the total charge in the system. In the presence of electroactive species in the electrochemical working cell, the applied potential will provoke a change in the concentration of the monitored electroactive species at the electrode surface by electrochemically reducing or oxidizing them. Changing the concentration of any electroactive participant at the working electrode surface will cause mass transport toward the electrode, and current will flow through the electrodes that is directly proportional to the analyte concentration. This simple dependence between measured current and analyte concentration makes voltammetric techniques to be routinely used for the quantitative determination of a variety of inorganic and organic compounds. Although there are many voltammetric techniques they are all based on the same electrochemical theory. Summarized here are some of the electrochemical laws common to all voltammetric techniques.

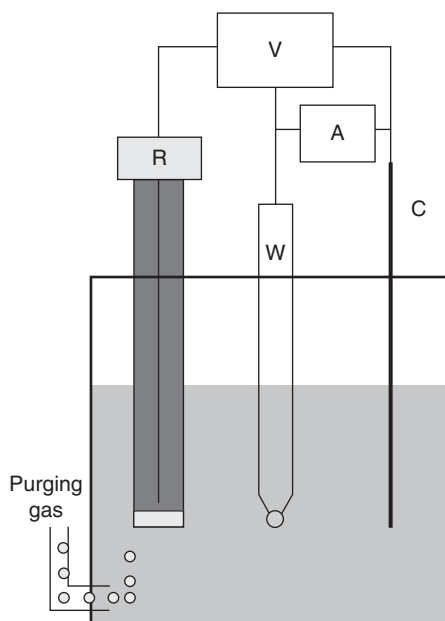
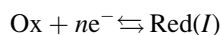


FIGURE 17.1 Schematic representation of a common electrochemical cell. R, reference electrode; W, working electrode; C, counter electrode; V, voltmeter; A, amperemeter.

17.3 THEORY AND DEFINITIONS IN VOLTAMMETRIC TECHNIQUES

Consider the simplest electrochemical reaction of the type



where Ox refers to the oxidized form of an electroactive substance initially present in the electrode cell, while Red is its reduced form (charges are omitted for the sake of simplicity), at least two well-known laws can be applied for expressing the interdependence between the applied potential and the surface concentrations of Ox and Red. For a thermodynamically reversible electrochemical reaction (i.e., a fast reaction where equilibrium is always reestablished as changes in electrode potential are made), the following type of Nernst equation always holds:

$$E = E^\theta + \frac{RT}{nF} \ln \frac{c(\text{Ox})_{x=0}}{c(\text{Red})_{x=0}}, \quad (17.1)$$

where

R is the gas constant (8.3144 J/mol K)

T is the absolute temperature (K)

n is the number of electrons exchanged

F is the Faraday constant (96,485 C/mol)

E^θ is the standard redox potential for the couple Ox/Red

For many electrochemical systems, especially for kinetics-controlled equations, the Butler–Volmer equation is often used:

$$\frac{I}{nFA} = k_s e^{-\alpha\varphi} [c(\text{Ox})_{x=0} - e^{\varphi} c(\text{Red})_{x=0}] \quad (17.2)$$

where

$$\varphi = nF(E - E^0)/RT$$

k_s is the standard rate constant of electron transfer

α is the electron transfer coefficient

A is the exposed (active) area of the working electrode

This equation is useful for estimating the heterogeneous standard rate constant of electron transfer k_s . When performing electrochemical experiments, applying a potential difference between the working and reference electrodes would alter the surface concentrations of both forms of the redox couple. This will cause a mass transfer toward (or from) the working electrode and current will flow through the cell. The current resulting from the electrochemical transformation of the electrochemically active species is known as faradaic current, and it is related to the material flux at the electrode–solution interface, as described by well-known Fick’s laws [1]. The instrumental output that is obtained in the voltammetric techniques is known as a voltammogram, which is a current–potential or I – E curve. The features of the obtained voltammograms depend on the type of the mass transfer phenomena, the number of exchanged electrons, the timescale of the measurement, as well as on the nature of the various coupled chemical reactions and surface phenomena that can happen in the electrochemical cell, and on the voltammetric technique used, in particular [1]. For analytical purposes, one is mainly interested to know the magnitude of the faradaic current of the voltammograms, which is a quantitative measure of concentration and the kinetics of the redox transformation of given electroactive species at the electrode surface. The magnitude of the faradaic current is a function of the analyte concentration, but it is also affected by additional factors, such as the size, shape, and material of the electrode, the solution resistance, the cell volume, and the number of electrons transferred in the electrode reaction [1].

17.4 INSTRUMENTATION IN VOLTAMMETRIC EXPERIMENTS

The modern electroanalytical system for voltammetric measurements are usually composed of three modules: a potentiostat, a personal computer, and an electrochemical cell (Figure 17.2). In some cases, the potentiostat and computer are packed into one part, whereas in most of the electrochemical systems the computer and the converters and microcontrollers are separate, so the potentiostat can operate autonomously.

17.4.1 POTENTIOSTAT

The potentiostat is considered as the “heart” of every electroanalytical instrumentation. In voltammetric techniques, the task of the potentiostat is to apply an exact potential and to observe the

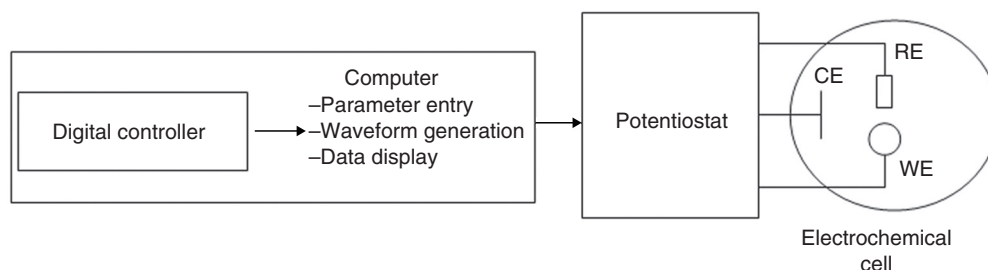


FIGURE 17.2 Simplified scheme of an electrochemical system designed for voltammetric measurements.

current changes in the system. In all modern electroanalytical instruments, the potentiostat package includes electrometer circuits, various converters and amplifiers, as well as microprocessors with internal memory. In older types of instruments, continuous linear change in the potential from one preset value to another was applied. However, all the modern potentiostats designed after 1980s operate in a digital (incremental) fashion. In these, a “staircase” modulated potential is generally used, with the “steps” having constant potential increment. The major benefits of staircase-modulated potentials are seen by the significant discrimination over the capacitive (nonfaradaic) currents [1]. Thanks to the digital fabrication of the applied potential, a wealth of pulsed voltammetric techniques have been designed [9], leading to increased sensitivity and much shorter times for performing experiments. The most frequent waveforms in modern potentiostats are linear scan, differential pulse, and square wave. Nowadays, various types of potentiostats can be found at the instrumentation markets, the size, power, and sophistication of which ranges from large research-grade instruments (10–30 kg with ± 30 V potential and 1 A–100 nA current ranges) to simple battery-powered units (3 to 1 kg with a ± 2.5 V potential and 6 mA–50 pA current ranges). Indeed, the type of voltammetric analysis, the required information, and the size of the electrodes are the main factors that will determine the choice of a particular instrument. While cyclic voltammetry can be performed with most of the commercially available potentiostats, quantitative tracing of some analytes requires use of microelectrodes and a sensitive voltammetric technique, which will be more expensive. Currently, several companies manufacture high-quality potentiostats capable of performing various voltammetric analyses. Among them, EG&G Princeton Applied Research, EcoChemie Netherlands, ACM Instruments, Cypress Systems, and Radiometer are the leaders. Along with the instrumentation, the manufacturer usually provides the software for data analysis, as well as the electrochemical cells and the electrodes. The problems with voltammetric procedures usually are related to a part of the system external to the instrument. In case of instrumental troubles, the first source of help should be someone with electrochemical experience. An instrument that operates well when it is set up is most likely to do so for many years. The main features of some of the commonly used potentiostats are given in Table 17.1.

AQ2

17.4.2 ELECTROCHEMICAL CELL AND ELECTRODES

An electrochemical cell is considered to be a sample holder, in which the corresponding analyte is dissolved in an appropriate solvent, and placed thereafter in an ionic electrolyte, where usually three electrodes (working, reference, and counter) are situated. The cells come commercially in various

TABLE 17.1

Manufacturing Data of Some Most Exploited Electroanalytical Instruments

Manufacturer	Potentiostat Model	Maximum Compliance Voltage (V)	Current Range	Web Site
Radiometer	PGZ100 (all-in-one)	± 30	30 pA–1A	www.radiometer-analytical.com
Princeton Applied Research	Versatile modular potentiostat (VSP)	± 20	1 nA–400 mA	www.princetonappliedresearch.com
EcoChemie	MicroAutolab III	± 30	1 nA–250 mA	www.ecochemie.nl
Cypress Systems	66-EI400 Bipotentiostat	± 10	10 pA–10 mA	www.cypresshome.com
Gamry Instruments	G 300 Potentiostat/ZRA	± 20	1 pA–300 mA	www.gamry.com
HEKA	PG 310	± 20	1 nA–2A	www.heka.com
Scribner Associates Incorporated	Multichannel microelectrode analyzer 900B	± 10	30 pA–100 mA	www.scribner.com
ACM Instruments	Gill-AC-Bi-Stat	± 15	10 pA–500 mA	www.acminstruments.com

designs, built mainly of glass, Teflon, or polyethylene material. The electrodes of the electrochemical system are usually all submerged in the electrochemical cell, whereas in some systems the reference electrode is placed in a separate compartment to avoid contamination, and it is connected to the cell via an electrolyte bridge.

The main criteria for an electrode to be classified as a reference electrode are to provide a reversible half-reaction with Nernstian behavior, to have a constant potential over time, and to be easy to assemble and maintain [10]. Among the most widespread reference electrodes used for experiments performed in aqueous solutions are the calomel electrode, whose potential is determined by the reaction $\text{Hg}_2\text{Cl}_2(\text{s}) + 2\text{e}^- \rightleftharpoons 2\text{Hg}(\text{l}) + 2\text{Cl}^-$, and the silver/silver chloride electrode (Ag/AgCl), whose potential is defined by the reaction $\text{AgCl}(\text{s}) + \text{e}^- \rightleftharpoons \text{Ag}(\text{s}) + \text{Cl}^-$. These electrodes are commercially available in a variety of sizes and shapes.

With respect to the counter electrodes, Pt wire, graphite, or a thin piece of gold are the common variants in most of the voltammetric techniques. The task of the counter electrode is to preserve electroneutrality in the system, which is done by the occurrence of an electrochemical reaction (usually H^+ reduction, or water oxidation) counter to that taking place at the working electrode.

A wide range of working electrodes are available. The metallic electrodes, such as Hg drops and Pt or Au disks, are among the most frequently used [11]. Mercury is very practical because of its highly negative overpotential for hydrogen ions reduction, and because of its constantly renewed surface [1,9,12]. Most electrochemical studies have been done using mercury as the working electrode, since it is equally adequate for studying the redox processes of inorganic and organic compounds as well as for elucidation of many surface phenomena, such as adsorption and crystallization. The main shortcoming with the mercury electrode is its low potential of oxidation (about +0.1 to +0.6 V depending on pH), because of which many compounds cannot be studied in the oxidation mode. Mercury can be used in different measuring modes such as hanging mercury drop electrode (HMDE) [13,14], DME [15,16], static mercury drop electrode (SMDE) [17], or even as mercury film electrodes [18,19]. Mercury is still being frequently used particularly for the analysis of metal ions and halides, and sulfide anions because of the possibility of amalgam formation in the former, and insoluble films in the case of the latter. Nowadays, because of mercury toxicity, the use of this electrode material is being restricted and the search is on for new electrode material.

AQ3

In last few decades, along with metallic electrodes, various modifications of carbon electrodes are also in use. Carbon electrodes are extremely lipophilic, and hence appropriate for studying the electrochemical features of lipophilic organic compounds. Carbon electrodes can also be found in a large variety of forms such as graphite composite electrodes [20], glassy carbon electrodes [21], carbon-paste electrodes [22,23], screen-printed electrodes [24], diamond electrodes [25], and bismuth-coated carbon electrodes [26], among others examples. Gold [27,28], bismuth films [29], biosensors [30], and immunosensors [31] are also part of the paraphernalia of electrode materials used with some advantage to solve analytical problems in food analysis.

17.5 SHORT REVIEW OF SOME COMMON VOLTAMMETRIC TECHNIQUES USED IN FOOD ANALYSIS

Numerous dynamic methods in electroanalytical chemistry have been developed in recent decades. Among them, the most familiar in food analysis are the cyclic voltammetric and the so-called pulse voltammetric techniques. Here we give a brief summary of some of these techniques.

17.5.1 CYCLIC VOLTAMMETRY

Cyclic voltammetry is one of the most exploited techniques in electrochemical studies. Its primary advantage comes from the fact that it gives insight into both the half-reactions taking place at the working electrode, providing at the same time information about the chemical or physical phenomena coupled to the studied electrochemical reaction [1,32,33]. Hence cyclic voltammetry is

often considered as electrochemical spectroscopy [32]. Although its usage is relatively minimal in quantitative food analysis, it is important to elaborate the principles of cyclic voltammetry, since every electroanalytical study almost inevitably commences with this technique. In cyclic voltammetry, starting from an initial potential E_i , a staircase (Figure 17.3a) potential sweep (or linear sweep in older potentiostats) is applied to the working electrode. After reaching a switching potential E_f , the sweep is reversed and the potential returns to its initial value. The main instrumental parameter in the cyclic voltammetry is the scan rate ($v = dE/t$), since it controls the timescale of the voltammetric experiment. The useful scan rates range from 1 to 1000 mV/s, although scan rates of over 10 V/s are technically achievable. The instrumental output in cyclic voltammetric techniques is a current–potential curve, a cyclic voltammogram (Figure 17.3b). The main features of the cyclic voltammogram are the cathodic and anodic peak potentials, the cathodic and anodic peak currents, and the formal (or half-peak) potential. While the half-peak potential (defined simply as a median between the cathodic and the anodic peak potentials) provides mainly thermodynamics information, the magnitudes of the peak currents reveal the kinetics involved in the electrochemical reaction. The shape of the cyclic voltammogram gives information about the type of the electrode reaction, the number of electrons involved in the elementary step of electrochemical transformation, as well as about the additional phenomena coupled to the electrochemical reaction of interest, like those for coupled chemical reactions or adsorption and crystallization [1,32]. If the electron transfer process is much faster than the kinetics of the mass transport processes (diffusion), then the electrode reaction is electrochemically reversible. In this case, the peak separation ΔE_p is defined as follows:

$$\Delta E_p = |E_{p,c} - E_{p,a}| = 2.303 \frac{RT}{nF}$$

For example, in a simple reversible and diffusion-controlled electrochemical reaction, where one electron is exchanged in an elementary act, the peak separation should be about 59 mV (at 25°C) [1]. Moreover, the peak potential separation should not vary by increasing the scan rate, while both cathodic and anodic peak currents should be a linear function of the square root of the scan rate. Every breach of these criteria means deflection of the electrochemical reversibility, caused either by the slow electron transfer (quasi-reversibility or irreversibility) or by additional involvement of the electroactive species in chemical reactions or adsorption phenomena. For an electrochemically

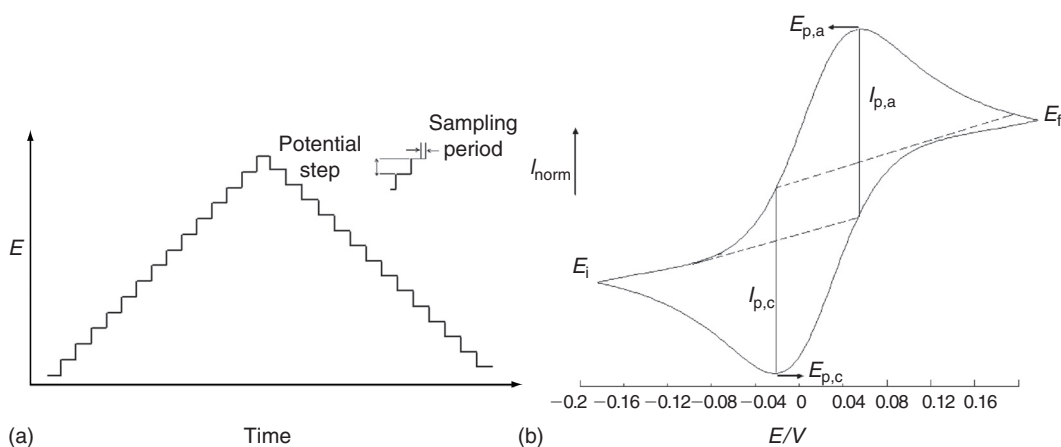


FIGURE 17.3 (a) Staircase potential ramp used in cyclic voltammetry, and (b) a cyclic voltammogram simulated for one-electron reversible charge transfer: $E_{p,c}$, cathodic peak potential; $E_{p,a}$, anodic peak potential; E_i , initial potential; E_f , switching potential; $I_{p,c}$, cathodic peak current; $I_{p,a}$, anodic peak current.

reversible reaction, the concentration of the electroactive species is linked to the peak current I_p by the Randles–Sevcik expression [1], and at 25°C it reads as follows:

$$I_p = 2.69 \times 10^5 n^{3/2} A c_0 \sqrt{D\nu}$$

where

A is the active electrode surface area

c_0 is the initial concentration of the electroactive species in the solution

D is its diffusion coefficient

n is the number of the electrons exchanged

ν is the scan rate

This equation enables exploration of cyclic voltammetry for quantitative determination purposes.

17.5.2 PULSE VOLTAMMETRIC TECHNIQUES

The invention of pulse voltammetric techniques was motivated by the fact that by changing the potential and measuring the current in a pulsed manner, a significant discrimination of the charging (non-faradaic) current can be achieved [1,9]. Applying the potential difference between the working and the reference electrodes in an electrochemical cell is a precondition for initiating an electron exchange between the working electrode and the electroactive species in the cell. However, this change in the potential difference also causes charging and discharging of the electrical double layer at the electrode–electrolyte interface, which initiates a flow of capacitive (charging) current too [1]. This current is undesirable for kinetic and analytical purposes, and efforts are being undertaken to minimize its contribution. The basis of all pulse techniques lies in the difference in the rate of the decay of the capacitive and faradaic currents following the potential steps. While the faradaic current decays with $t^{-1/2}$ for diffusion-controlled electrode reactions, for the same reactions, the capacitive current decays exponentially with time. Accordingly, by sampling the currents at the end of the applied potential pulses, one gets negligible capacitive currents, yet significant faradaic currents [34]. In this way, the sensitivity of the voltammetric method will be significantly increased, and the measured current will refer almost exclusively to the faradaic reaction of interest. In novel electrochemical instruments, one meets various pulse voltammetric techniques, which differ in the pulse-wave form and the way by which the current is sampled. The most important parameters of all pulse voltammetric techniques are as follows: (1) pulse amplitude, which is the height of the potential pulse, (2) pulse width, which is the duration of the potential pulse, and (3) sampling period, defined as a time at the end of the potential pulse in which current is measured. We refer to some of the most important pulse techniques in this chapter.

17.5.2.1 Normal Pulse Voltammetry

In normal pulse voltammetry (NPV), a series of potential pulses with constant width and permanent increased amplitude are applied, with the potential returning to the initial value after each pulse [9]. The current is measured in a certain period at the end of each pulse, which is enough to diminish significantly the charging current component (Figure 17.4a). The duration of the pulses ranges from 1 to 200 ms, while the interval between the pulses is several seconds. The instrumental output in this technique is an I – E curve (normal pulse voltammogram), with sigmoidal shape (Figure 17.4b) as it is commonly obtained in classical (normal) polarographic techniques [1]. Hence this technique is called “normal” pulse voltammetry.

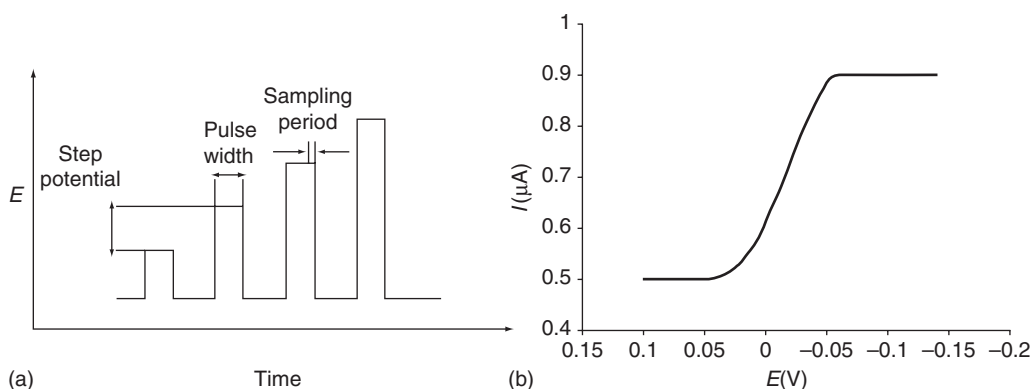


FIGURE 17.4 (a) Potential form and (b) resulting simulated voltammogram in normal pulse voltammetry.

AQ4

17.5.2.2 Differential Pulse Voltammetry

The potential form in differential pulse voltammetry (DPV) consists of small pulses of constant amplitude (10–100 mV) superimposed on a staircase-wave form. The current in this technique is measured twice in each pulse period, first at potential at the beginning of the applied pulse, and second at the ending of the same pulse (Figure 17.5a) [34]. The measured current in the instrumental output, referred to as differential pulse voltammogram (Figure 17.5b), is actually the difference between the currents measured for each single pulse. The current measured thus enables one to obtain much higher sensitivity of DPV with respect to NPV.

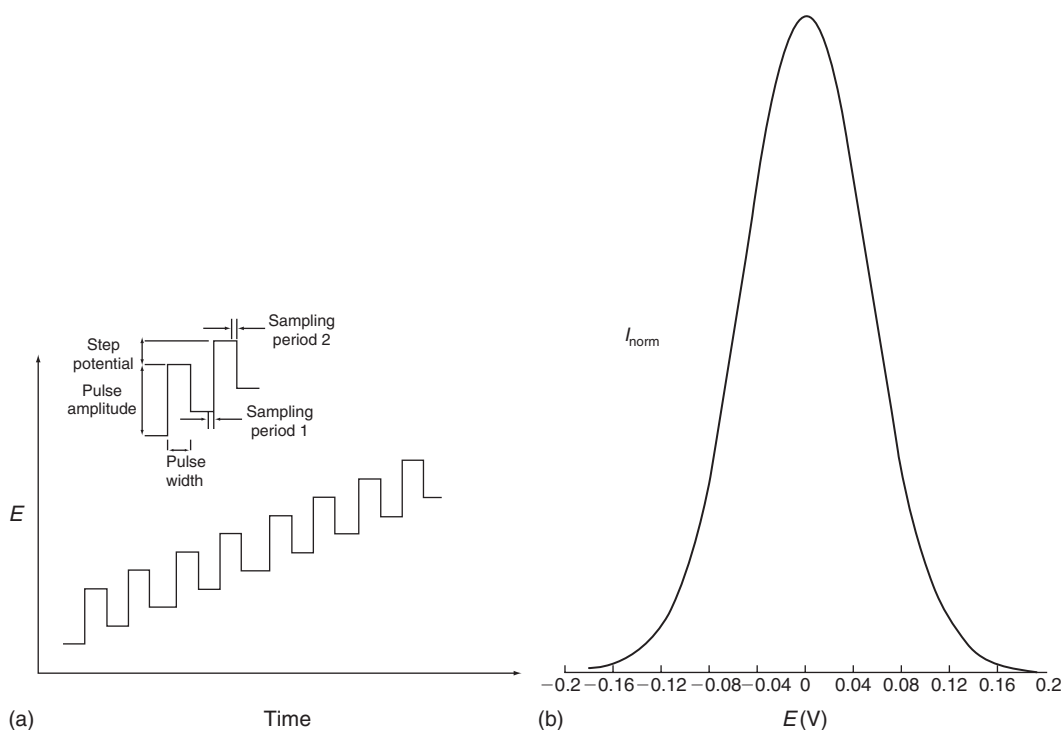


FIGURE 17.5 (a) Potential form and (b) resulting simulated voltammogram in differential pulse voltammetry.

17.5.2.3 Square-Wave Voltammetry

Square-wave voltammetry (SWV) is the most advanced and the most sophisticated technique in the family of pulse voltammetric techniques [10,35,36]. The potential form in SWV consists of symmetrical square-wave pulses with constant amplitude E_{sw} , which are superimposed on a staircase-wave form (Figure 17.6a). The potential in SWV changes for a constant potential step dE . The current in this technique is measured twice at the end of each half cycle. The currents measured at the end of oxidation half cycles give the oxidative (forward) current component, while the currents measured at reduction half cycles give the reduction (backward) current component (Figure 17.6b). The net current in SWV is obtained as a subtraction between the forward and the backward currents. However, since the reductive currents (by convention) have a negative sign, the net current in SWV is actually a sum of the absolute values of both the current components (Figure 17.6b). This method of measurement makes SWV the most sensitive electroanalytical technique. The net peak current in SWV, as in other pulse voltammetric techniques, is proportional to the analyte concentration, resulting often in detection limits in sub-nanomolar ranges. Besides, SWV provides an insight into both the half-electrode reactions, thus having a distinct advantage over cyclic voltammetry for studying the mechanisms of electrochemical reactions. SWV is a very fast technique, providing insight into the kinetics of fast electron transfer reactions, and into the kinetics of rapid chemical reactions coupled to the electroactive species. Although the theory of SWV is still developing, many excellent theoretical papers on SWV have appeared in last 30 years, providing criteria for recognition of many complex electrode mechanisms, and providing methods for measuring the kinetics and thermodynamics of various processes encountered in the investigated electrochemical systems [1,9,35]. During the last 25 years, this has led to SWV becoming one of the most explored voltammetric techniques for both quantitative applications and mechanistic studies, as well as for the determination of kinetics and thermodynamics in various electrochemical systems.

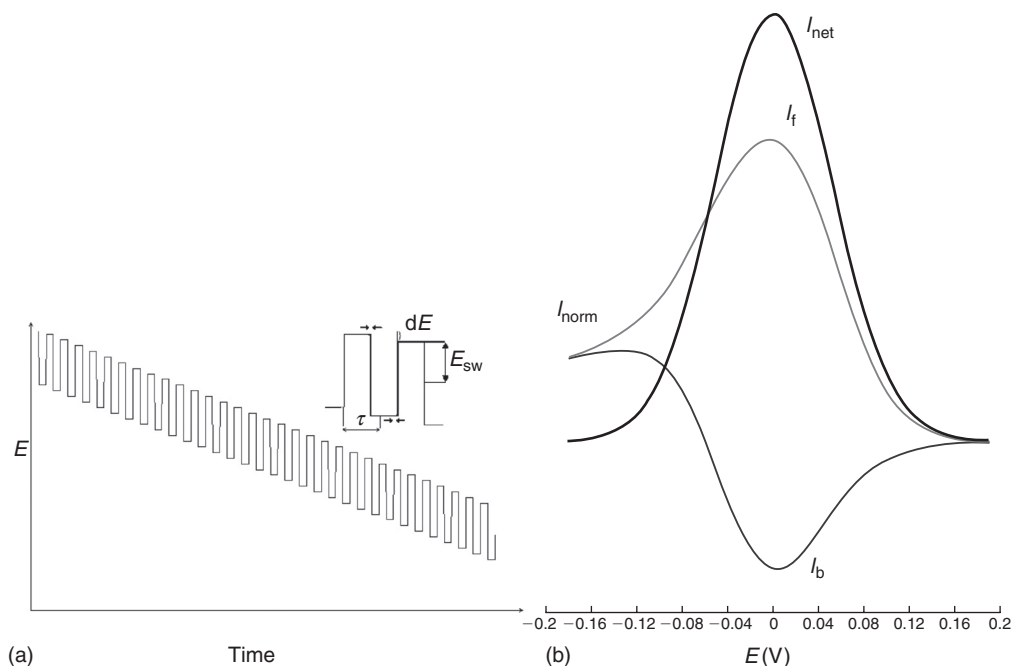


FIGURE 17.6 (a) Potential form in square-wave voltammetry: E_{sw} , potential amplitude; dE , potential step; τ , duration of a single pulse. The current is sampled twice in each pulse, in the time period between two arrows at the inset; (b) resulting simulated voltammogram in square-wave voltammetry: I_f , forward current, I_b , backward current, I_{net} , net current.

17.6 PRECONCENTRATION VOLTAMMETRIC TECHNIQUES

The goal of every analytical technique is to provide lower detection limits, good sensitivity, and good selectivity. In all voltammetric techniques, the detection limits depend mainly on the nature of mass transport phenomena, as well as on the nature and features of the electrode and the electro-active species. If mass transport occurs only by diffusion, then the detection limits usually range around micromolar concentrations [1]. However, many organic compounds exhibit surface-active properties, which are manifested by their adsorption from the solution to the electrode surface. Many other compounds are capable of dissolving or reacting with the electrode material (usually with the mercury electrode), forming an amalgam or a sparingly soluble mercury complex, respectively. These phenomena are bases for developing preconcentration techniques, such as adsorptive stripping voltammetry (AdSV), the anodic (ASV) and the cathodic (CSV) stripping voltammetric methods, respectively. The mercury electrode is one of the mostly used working electrode in stripping voltammetric techniques, while examples exist where other metallic modified electrodes have been also explored [12]. Stripping voltammetric techniques are among the most sensitive for trace analysis. Examples are known where detection limits below picomolar range have been reported by using some of the stripping voltammetric modes [37–39]. To obtain reproducible results, the following important conditions must be taken into account in all stripping techniques: constancy of the electrode surface, invariable rate of stirring, and constant deposition time. We give here a brief summary of the most frequently used preconcentration voltammetric techniques.

17.6.1 ADSORPTIVE STRIPPING VOLTAMMETRY

Adsorptive stripping voltammetry (AdSV) is one of the most sensitive voltammetric techniques, which has been successfully applied for the determination of traces of various compounds at sub-nanomolar levels [1,12,39]. AdSV is based on previous accumulation (by adsorption) of the compound on the working electrode at some adequate constant potential, and consecutive electrolysis (oxidation or reduction) of the adsorbed material. It is well known that many organic and inorganic anions have a tendency of adsorbing at the mercury electrode [39], which is a prerequisite step for their accumulation. Besides the mercury electrode, which is commonly used as a working electrode in adsorptive stripping techniques [39], another type of accumulation can be achieved with a chemical interaction between the analyte and the modified electrode surfaces of another (non-mercury) type of working electrode [1,12]. Along with the electrode material and the accumulation time, the choice of the accumulation potential is a very important factor that leads to the substantial increase of sensitivity for a particular ASV. As the working voltammetric technique in AdSV, the DPV and SWV are commonly used [12]. As with other stripping techniques, attention must be paid to sample preparation and avoidance of possible contaminations, since these techniques are extremely sensitive to various impurities.

17.6.2 ANODIC STRIPPING VOLTAMMETRY

Anodic stripping voltammetry (ASV) finds enormous practical use for the determination of trace of various metals [1,12,40]. It is well known that many metals can form amalgams with mercury (i.e., to dissolve in it). By applying sufficient negative potentials for a prolonged electrolysis time, the reduction of the present metal ions from the solution takes place, and subsequent concentration of the metals into the mercury electrode is achieved. Such amalgamated, the metals are thereafter stripped off (oxidized) from the mercury electrode, when running the potential in positive (anodic) direction. Their dissolution process is depicted in voltammetric peaks, with positions at the potential scale depending on the nature of the metals. The resulting peak currents of the voltammetric responses are proportional to the metal ion concentrations in the solutions. With ASV, it is possible to determine simultaneously several metal ions (up to six), if their standard redox potential differs

AQ5

for at least 200 mV. This technique also achieves low detection limits, frequently in the nanomolar range. The main shortcoming of this technique is the possibility of formation of intermetallic compounds, like ZnCu for example, which can lead to misinterpretation of voltammetric responses. Overlapping stripping peaks caused by similarity in oxidation potential or the presence of surface-active organic compounds that adsorb on the mercury surface and inhibit metal deposition can also introduce difficulties in the implementation of this technique. However, such problems may be avoided by adjusting the deposition potential.

17.6.3 CATHODIC STRIPPING VOLTAMMETRY

Cathodic stripping voltammetry (CSV) is a technique of choice when the investigated compounds are capable of reacting with the mercury ions of the mercury electrode, forming sparingly soluble salts at the surface of the working electrode [1,3,12,41–43]. Initially, by applying a positive potential for a certain time, an insoluble film, created by chemical reaction between the investigated compound and the mercury ions at the surface of the working (mercury) electrode, will be formed. In the second step, this film is stripped off by running the potential in the negative (cathodic) direction. This method has been explored for quantitative determination of many inorganic anions, such as halides, sulfides, selenides, as well as for many biologically active compounds (amino acids, proteins, nucleic acids, etc.) containing groups that can react with the mercury ions [3,12,41–43]. Generally, the compounds containing Cl, F, Br, SH, and SeH groups are potentially cathodic-stripping active species [12]. The main advantage of this technique is its employment for the determination of electrochemically inactive compounds, i.e., compounds that do not show electrochemical activity in the given potential range [41].

17.7 ELECTROCHEMICAL TECHNIQUES IN FOOD ANALYSIS

A large number of examples of electrochemical methods developed and applied to a vast number of compounds relevant to food industry and food quality can be found in the literature. However, here we select only papers where electrochemical techniques have been directly applied to food analysis. Some valuable review papers can be found on the use of stripping voltammetry [3], biosensors [44–46], and speciation of arsenic [47] in food analysis.

17.7.1 FOOD COLORANTS

Electrochemistry of azo compounds was first reported by Florence in 1974 [48]. The first description of the use of electrochemical techniques for food colorant analysis was published in 1979 by Fogg and Yoo [49]. This work describes the methodology for the determination of tartrazine, amaranth, green S, and sunset yellow FCF analysis in orangeade, limeade, and black currant health drinks by differential pulse polarography (DPP). Strategies for simultaneous determination of colorants in fruit juices can also be found [50]. Several others works dealing with the electrochemical determination of colorants and flavors can be found in the literature and some of them are listed in Table 17.2 [51–57].

17.7.2 METAL CONTAMINANTS

Although trace amounts of metal ions in food products play an essential role in metabolic processes, they can easily surpass the toxicity limits and therefore the importance of established health and risk regulations [58]. Voltammetry and in particular methods that involve stripping stages are well fitted for metal analysis in food as the numerous references found in the literature demonstrate (Table 17.3) [59–78]. Two main procedures are adopted in these analysis: ASV for those metals that can easily form amalgams with mercury, namely Pb, Zn, Cu, Cd, Sb, Tl, and Hg (in gold or carbon electrodes), and adsorptive CSV for other metal ions such as Al, Cr, Co, Fe, Ni, Ti, or U.

AQ6

TABLE 17.2
Overview of the Methods and Electrodes in Voltammetric Determination of Some Colorants in Drinks

Colorant	Method	Electrode	Sample	Reference
Allura red	DPP	Hg	Sweets and soft drinks	[50]
	DPP	Hg	Soft drinks	[52]
Amaranth	DPP	Hg	Soft drinks	[47]
	AdSV	HMDE	Soft drinks	[48]
Azorubin	DPP	Hg	Soft drinks	[52]
Brilliant blue FCF	CSV	HMDE	Soft drinks	[55]
Carmoisine	DPP	Hg	Sweets and soft drinks	[50]
Erythrosine	CSV	HMDE	Soft drinks	[55]
Green-S	DPP	Hg	Soft drinks	[47]
Indigo-carmin	CSV	HMDE	Sweets and juices	[49]
Patent Blue V	DPV	NGCE	Soft drinks, liquors	[19]
Ponceau 4R	AdSV	HMDE	Soft drinks	[48]
	DPP	Hg	Sweets and soft drinks	[50]
	DPP	Hg	Soft drinks	[52]
Quinoline yellow	CSV	HMDE	Soft drinks	[55]
Sunset yellow	AdSV	HMDE	Soft drinks	[48]
	DPP	Hg	Soft drinks	[53]
	ASSWV	Hg	Soft drinks	[54]
Sunset yellow FCF	DPP	Hg	Soft drinks	[47]
Tartrazine	DPP	Hg	Soft drinks	[47]
	AdSV	HMDE	Soft drinks	[48]
	CSV	HMDE	Sweets and soft drinks	[49]
	ASV	HMDE	Soft drinks	[51]
	DPP	Hg	Soft drinks	[53]

Note: DPP, differential pulse polarography; AdSV, adsorptive stripping voltammetry; HMDE, hanging mercury drop electrode; CSV, cathodic stripping voltammetry; DPV, differential pulse voltammetry; NGCE, ASSWV, ASV, anodic stripping voltammetry.

AQ7

17.7.3 PESTICIDES AND HERBICIDES

Pesticides and herbicides represent a major concern in food quality assurance. Voltammetry can be a useful tool for their analysis since most of the organic compounds used for pest and herb control have electroactive groups. Some recent reviews can give a good highlight of electrochemical methods for determination of herbicides and pesticides [79–81]. Hance was the pioneer in the use of electroanalytical techniques for pesticide residue analysis [82]. In his work, Hance describes the behavior of 38 herbicides using derivative polarography, showing that 28 of them were electroactive. The well-known inhibition effect of pesticides over enzymes is also explored to build electrochemical sensors for pesticide analysis (see Section 17.7.4). Pesticides have different electroactive groups and some of them require derivatization before determination. Triazines present one or more reduction peaks corresponding to the reduction of mono- and biprotonated forms. For *s*-triazine, reduction occurs at the $-C=N-$ bond of the heterocyclic ring [83]. The mechanism of reduction of asymmetrical triazines depends on the structure of the molecule. As an example, guthion is reduced in the $-N=N-$ bond of the heterocyclic ring [84], and reduction of metamitron involves the functions $-C=N-$ and $N-NH_2$ that are present in the molecule [85]. Mercury [86] electrodes are commonly used for the electrochemical determination of triazines; however, more recently, biosensors have also been employed in the determination of triazines in food [87].

AQ8

TABLE 17.3
Overview of the Methods and Electrodes Used in Voltammetric Determination of Some Metals in Food

Metal	Sample Treatment	Sample	Method	Electrode	Reference
As(III)	Acid digestion	Biological material	ASV	Au	[57]
Se(IV)	Digestion	Pig kidney (BCRNo. 186 certified selenium content)	ASV	Au	[58]
Se(VI)	Digestion	Pig kidney (BCRNo. 186 certified selenium content)	ASV	Au	[58]
Hg(II)	—	Alcoholic drinks	ASV	Au	[59]
Cd(II)	—	Meat and egg powder	CAdSV	HMDE	[60]
Cu(II)	Digestion	Cow's liver tissue	CAdSV	HMDE	[61]
Ni(II)	—	Canned vegetables	CAdSV	HMDE	[62]
Cd(II)	—	Beer	SSWASV	MTFE	[63]
Pb(II)	—	Beer	SSWASV	MTFE	[63]
Fe(II)	Acid digestion	SRM-1547 from peach leaves	OSWV	SGE	[64]
Sn(IV)	—	Juice and canned fruit	LSASV	MTFE	[65]
Pb(II)	—	Juice and canned fruit	LSASV	MTFE	[65]
Mo(VI)	UV irradiation, dry-ashing	Biological material	CSV	MTFE	[66]
U(VI)	—	Sugar	CSV	GCE	[67]
Sn(IV)	—	Canned fruit drinks and juices	ASV	CCE	[68]
Pb(II)	—	Canned fruit drinks and juices	ASV	CCE	[68]
Cu(II)	—	Whisky	ASV	μ Pt	[69]
Pb(II)	Solubilization	Edible oils	ASV	MTFE	[70]
Cu(II)	Solubilization	Edible oils	ASV	MTFE	[70]
Cd(II)	Solubilization	Edible oils	ASV	MTFE	[70]
Cu(II)	—	Beer	ASV	GCE	[71]
Pb(II)	—	Milk	LSV	SMFE	[72]
Pb(II)	—	Wine	ASV	MF μ E	[73]
Cu(II)	—	Wine	ASV	MF μ E	[73]
As(V)	MWAAD	Tobacco leaves, nettles	CSV	HMDE	[74]
As(III)	MWAAD	Tobacco leaves, nettles	CSV	HMDE	[74]
As(V)	Acid digestion	Zinc oxide as food additive used in feed	CSV	HMDE	[75]
As(III)	Acid digestion	Zinc oxide as food additive used in feed	CSV	HMDE	[75]

Note: MWAAD—, ASV—anodic stripping voltammetry, CAdSV—, SSWASV—, OSWV—, LSASV—, CSV—cathodic stripping voltammetry, LSV—, HMDE—hanging mercury drop electrode, MTFE—, SGE—, GCE—, CCE—, SMFE—, MF μ E—.

AQ9

The redox process of organophosphates presents a well-defined process at neutral, acid or, basic media, which is attributed to the reduction of the C=C bond or to the reduction of chloride or nitro groups presented in the pesticide structure [88]. The use of gold microelectrodes [89], mercury electrodes [90], and biosensors have been reported for the analysis of organophosphate pesticides [30]. Metabolites of organophosphate pesticides (e.g., *p*-nitrophenol) can be also used in electrochemical methodologies for the indirect analysis of organophosphate pesticides [91].

The reduction mechanism of pesticides with nitropesticides is associated with the reduction of the nitro group with consequent formation of hydroxylamines or further to the corresponding amines and is currently a well-defined process [92]. As with the triazines, some of these pesticides containing nitro groups can be adsorbed onto the surface of mercury electrodes [93] or as an alternative can be analyzed by using biosensors [94].

Carbamates represent a large number of insecticides and herbicides. Some of the carbamates require a derivatization step before their electrochemical determination or analysis of their residues; however, the use of biosensors usually solves this difficulty [30]. Adsorption at gold electrode is also used for the direct analysis of disulfiram in peas [95].

Another important class of pesticides is the bipyridium pesticides also known as “viologens.” Not all the pesticides in this family can be reduced at an electrode surface. From mechanistic studies, it seems that an important condition is the coplanarity of the two heterocyclic nuclei with the electrode surface [96]. Analysis of paraquat in foodstuff using gold microelectrodes have been successfully carried out [27,97].

Organochloride pesticides are part of another important family of pest control chemicals. Several electrochemical studies were consistent in their conclusion of a reaction mechanism involving the removal of one atom of chlorine [17]. The adsorption of organochloride pesticides at the mercury electrode and other metallic electrodes can impair the sensitivity and reproducibility of measurements. The addition of surfactants or the use of micellar systems seems to improve the signal-to-noise ratio [98]. This methodology demonstrated the presence of several organochloride pesticides in apples.

Pyrethroids are insecticides originally extracted from natural sources. In the case of deltamethrin, the compound exhibits a single well-defined peak because of the reduction of the $-C=C-$ moiety at the mercury electrode. The analysis of deltamethrin in vegetables and cereals has been reported [99]. Analysis of other classes of pesticides such as xylylalanine, dicarboximide, azole, anilide, and strobil have also been reported in the literature [30].

Table 17.4 presents a list of works reporting the determination of a large number of pesticides, indicating a large diversity of matrixes [100–110] and electrode materials. Although sulphonylureas and phenylureas constitute an important group of pest control chemicals with redox activity and

TABLE 17.4
Overview of the Methods and Electrodes Used in Voltammetric Determination of Some Pesticides in Food

Pesticide		Electrode	Matrix	Reference
Fenhexamid	Anilide	Biosensor	Fruits	[30]
Myclobutanil	Azole	Biosensor	Fruits	[30]
Propiconazol	Azole	Biosensor	Fruits	[30]
Paraquat	Bipyridinium	Au UME	Fruits, potatoes, and sugar cane	[27]
Paraquat	Bipyridinium	Au UME	Fruit juice	[97]
Aldicarb	Carbamates	Biosensor	Vegetables	[103]
Aldicarb	Carbamates	Biosensor	Fruits and vegetables	[104]
Carbaryl	Carbamate	Biosensor	Milk	[100]
Carbaryl	Carbamates	Vitreous carbon	Vegetables	[102]
Carbaryl	Carbamates	Biosensor	Kiwi	[105]
Carbaryl	Carbamates	Biosensor	Vegetables	[103]
Carbaryl	Carbamates	Biosensor	Egg	[94]
Carbaryl	Carbamates	Biosensor	Meat	[94]
Carbaryl	Carbamates	Biosensor	Milk	[94]
Carbaryl	Carbamates	Biosensor	Honey	[94]
Carbaryl	Carbamates	Biosensor	Fruits and vegetables	[104]
Carbaryl	Carbamates	Biosensor	Fruits	[30]
Carbofuran	Carbamates	Biosensor	Fruit juice	[101]
Carbofuran	Carbamates	Vitreous carbon	Vegetables	[102]
Carbofuran	Carbamates	Biosensor	Vegetables	[103]
Carbofuran	Carbamates	Biosensor	Fruits, vegetables, and dairy products	[106]

(continued)

TABLE 17.4 (continued)
Overview of the Methods and Electrodes Used in Voltammetric Determination of Some Pesticides in Food

Pesticide		Electrode	Matrix	Reference
Carbofuran	Carbamates	Biosensor	Fruits and vegetables	[104]
Disulfiram	Carbamates	Au UME	Peas	[95]
Disulfiram	Carbamates	Modified graphite	Strawberry	[107]
Ethiofencarb	Carbamates	Biosensor	Fruits	[30]
Methomyl	Carbamates	Biosensor	Vegetables	[103]
Methomyl	Carbamates	Biosensor	Fruits and vegetables	[104]
Pirimicarb	Carbamates	Biosensor	Fruits	[30]
Promecarb	Carbamates	Vitreous carbon	Vegetables	[102]
Propoxur	Carbamates	Vitreous carbon	Vegetables	[102]
Propoxur	Carbamates	Biosensor	Vegetables	[103]
Propoxur	Carbamates	Biosensor	Fruits and vegetables	[104]
Thiram	Carbamates	Modified graphite	Strawberry	[107]
Methiocarb	Carbamates	Biosensor	Fruits	[30]
Iprodion	Dicarboximide	Biosensor	Fruits	[30]
Dinoseb	Nitropesticides	Mercury film	Fruit juice	[93]
Methyl parathion	Nitropesticides	Biosensor	Egg	[94]
Methyl parathion	Nitropesticides	Biosensor	Meat	[94]
Methyl parathion	Nitropesticides	Biosensor	Milk	[94]
Methyl parathion	Nitropesticides	Biosensor	Honey	[94]
Dieldrin	Organochloride	HMDE	Apples	[98]
Endosulfan sulphate	Organochloride	HMDE	Apples	[98]
Heptachlor	Organochloride	HMDE	Apples	[98]
Sulfan	Organochloride	HMDE	Apples	[98]
~ α -Endosulfan	Organochloride	HMDE	Apples	[98]
β -Endosulfan	Organochloride	HMDE	Apples	[98]
Clorofenvinphos	Organophosphate	DME	Cereals	[90]
Crotoxyphos	Organophosphate	DME	Cereals	[90]
Dicrotophos	Organophosphate	DME	Cereals	[90]
Paraoxon	Organophosphate	Biosensor	Baby food	[30]
Paraoxon	Organophosphate	Biosensor	Fruit juice	[101]
Paraoxon	Organophosphate	Biosensor	Kiwi	[105]
Coumaphos	Organophosphate	Biosensor	Grape juice	[108]
Chloropyrifos-methyl	Organophosphate	Biosensor	Grape juice	[108]
Paraoxon	Organophosphate	Biosensor	Milk	[100]
Dichlorvos	Organophosphate	Biosensor	Wheat	[109]
Dichlorvos	Organophosphate	Biosensor	Wheat	[110]
Deltamethrin	Pyrethroid	HMDE	Vegetables and cereals	[99]
Esfenvalerat	Pyrethroid	Biosensor	Fruits	[30]
Azoxystrobin	Strobin	Biosensor	Fruits	[30]
Desmetryne	Triazines	HMDE	Fruit juice	[86]
Simazine	Triazines	Biosensor	Meat	[87]
Simazine	Triazines	Biosensor	Vegetables	[87]
Simazine	Triazines	Biosensor	Milk	[87]
Simazine	Triazines	Biosensor	Fruit juice	[87]
Piperonylbutoxid	Unclassified	Biosensor	Fruits	[30]
Metalaxyl	Xylalalanine	Biosensor	Fruits	[30]

Note: UME—, HMDE—hanging mercury drop electrode, DME—.

AQ10

AQ11

albeit there are some works reported on their electrochemical behavior [111], it was not possible to find any paper describing their determination in natural or processed food products.

One drawback of biosensor strategy that uses enzyme inhibition by pesticides is the fact that it is not specific and cannot be used to identify the pesticide or herbicide per se but solely to identify their presence [112]. The advantage of using the biosensor is that it allows a fast and cheap method for pesticide detection, and hence can be used for screening purposes.

17.7.4 BIOSENSORS

A general definition of biosensors includes all devices that incorporate a biological or biologically derived sensing element, which is usually associated with a transducer. The main advantage of the biosensors is to take benefit of thousands of years of evolution that made available biological macromolecules that react specifically with the target analyte. The primary aim of a biosensor is to produce a signal that can be related to a specific analyte. Biosensors have proven to be a good analytical tool well-fitted to cope with the challenges that food analysis gives rise to, and several books and review papers are available on biosensors [113–116]. As biosensors use different transducing modes [117] they can surpass the demanding requirements found when dealing with difficult matrixes and tough standards currently found in food analysis. Two main groups of biosensors can be identified: (1) those dealing with direct measurement of the analyte or a product of the enzymatic reaction, and (2) those dealing with the indirect quantification of the analyte evaluating the decrease in the electrochemical signal of the biosensor caused by the poisoning of the sensor element when the analyte is present (e.g., contaminant [29], insecticide [28]). Amperometric biosensors rely on the current intensity generated at the working electrode (either its increase in case of direct measurements, or its decrease for indirect measurements) after the analytes interact with an enzyme. According to the electrochemical process used for transduction, the biosensors are usually classified into four main groups: oxygen electrodes (when the oxygen consumption during the enzymatic reaction is assessed) [118], peroxide electrode (when the oxygen peroxide formed during the enzymatic reaction is monitored) [119], redox mediators, and NADH electrochemical sensors (electrocatalytic detection based on the recycling of redox mediators, most of them involving the use of NADH in the recycling step) [120,121].

AQ12

17.7.5 OTHER APPLICATIONS

Although not major but significant, electrochemical methods also contribute to the determination of other analytes with prime importance for food analysis such as antibiotics (ceftazidime in milk by differential pulse CSV [122]), possible human carcinogens (butylated hydroxyanisole in potato chips [20]), flavors or flavor enhancers (vanillin in vanilla sugar, chocolate biscuits, and chocolate [18], inosinic acid in dehydrated soups [123], diacetyl in beer [124], and α -diketones in brandy, vinegar, wine, and butter samples [125]), antidepressants in herbal medicinal products [126], *tert*-butylhydroquinone in popcorn [127], hormones (progesterone in milk [128]), and polychlorinated biphenyls (PCBs) in meat and milk [129].

17.7.6 HYPHENATED TECHNIQUES

A large percentage of food analysis relies on the measurement of a vast number of chemicals and parameters that make use of chromatographic techniques. Electrochemistry can also play an important role in the detection of the analytes in chromatographic analysis either in high-performance liquid chromatography or in electrophoresis. Electrochemical detectors present detection limits (5–50 ng/mL) very similar to those of fluorescence detectors (5–500 ng/mL) and much better than ultraviolet detectors (1–20 μ g/mL) [130]. Examples of the use of electrochemical detectors are the determination of amino acids and sugars in rice wine [131], heterocyclic aromatic amines in beef

extract [132], nitrite [133] and nitrate [125] in meat products, organic acids in red wine by ion-exclusion chromatography [134], taurine in plant extracts, milk powder, and health beverages, flavonoids and vitamin E isomers in seeds and nuts [5], isoflavones in soybean food [135], vitamin A in cereals [136], alkaloids in foods [117], heterocyclic aromatic amines in food flavors [118], heterocyclic aromatic amines in commercial beef extract [137], mutagenic or carcinogenic compounds in charcoal-grilled meat [138], nitrofurans derivatives in milk [139], ascorbic acid in athletes food, nutritional supplement, infant milk [140], aldehydes in honey, coffee, refreshments, sherry, port, dry fruits, and breakfast cereals [141], nitrite and nitrate in fish and meat products [142], and coenzymes in fish, meat, and rye flour [143].

17.8 NEW TRENDS

The requirements for highly precise and fast quantification of many important compounds by food analysis lead to the rapid development of various electrochemical sensors. Indeed, the future of electrochemical techniques applied in food analysis is to enable simultaneous analysis for several compounds. Demanding electrochemical applications require high-performance instrumentation coupled with high-throughput capabilities. It is recognized that electrochemical sensor development has equipment demands that are sometimes hard to satisfy with conventional potentiostats. To address these applications, various multichannel instruments are starting to appear in the electrochemical instrumentation market. Each channel of these potentiostats can be controlled independently or used in conjunction with other channels (potentiostats) to perform the same experiment on different electrodes. In addition, up to 20 channels can be used with one reference and one counter electrode (the so-called N'stat mode). Each potentiostat is capable of at least 20 V scan ranges, 400 mA current capabilities with 20 V compliance, and a timebase of 200 μ s. This is a critical feature for multielectrode potentiostatic and potentiodynamic pitting experiments. Certainly, the successful employment of multichannel potentiostats in food analysis is closely tied with the development of highly specific sensors. Only in this way can electrochemical techniques compete with other techniques currently used intensively in food analysis, for example, chromatographic techniques.

Although important, there has been no research effort in recent years on the application of novel electrode materials and electrochemical techniques into the electrochemical detectors in chromatographic analysis, and this can be a field of fruitful research in the near future.

REFERENCES

1. Bard, A.J. and Faulkner, L., *Electrochemical Methods*, Wiley, New York, 2001.
2. Bagotsky, V.S., *Fundamentals of Electrochemistry*, 2nd ed., Wiley, New York, 2005.
3. Brainina, Kh.Z., Malakhova, N.A., and Stojko, N.Y., Stripping voltammetry in environmental and food analysis, *Fresenius J. Anal. Chem.*, 368, 307, 2000.
4. Antropov, L.I. and Beknazarov, A., *Theoretical Electrochemistry*, University Press of the Pacific, 2001.
5. Codognoto, L. et al., Electroanalytical and chromatographic determination of pentachlorophenol and related molecules in a contaminated soil: A real case example, *Microchem. J.*, 77, 177, 2004.
6. Tsai, Y.C. et al., Microwave-enhanced anodic stripping detection of lead in a river sediment sample. A mercury-free procedure employing a boron-doped diamond electrode, *Electroanalysis*, 13, 831, 2001.
7. Delgado-Zamarreño, M.M. et al., Pressurized liquid extraction prior to liquid chromatography with electrochemical detection for the analysis of vitamin E isomers in seeds and nuts, *J. Chromatogr. A*, 1056, 249, 2004.
8. Xu, Q. et al., Application of a single electrode, modified with polydiphenylamine and dodecyl sulfate, for the simultaneous amperometric determination of electro-inactive anions and cations in ion chromatography, *J. Chromatogr. A*, 997, 65, 2003.
9. Osteryoung, J.G. and Schreiner, M.M., Recent advances in pulse voltammetry, *CRC Crit. Rev. Anal. Chem.*, 19, S1, 1988.

AQ13

10. Kahlert, H., Reference electrodes, in *Electroanalytical Methods*, Scholz, F. (Ed.), Springer, Berlin/Heidelberg/New York, 2001, chap. III. AQ14
11. Komorsky-Lovric, S., Working electrodes, in *Electroanalytical Methods*, Scholz, F. (Ed.), Springer, Berlin/Heidelberg/New York, 2001, chap. III.
12. Wang, J., *Analytical Electrochemistry*, 3rd ed., Wiley-VCH, 2006.
13. Castrillejo, Y. et al., Determination of food additive azo dyes at an HMDE with adsorptive stripping voltammetry, *Electroanalysis*, 2, 553, 1990.
14. Qiong, L. et al., Determination of trace aluminum in foods by stripping voltammetry, *Food Chem.*, 97, 176, 2006.
15. Inam, R. and Toprak, C., Polarographic determination of some toxic trace elements in fish muscles, *Fresenius Environ. Bull.*, 14, 489, 2005.
16. Obendorf, D. and Reichart E., Determination of hesperidin by cathodic stripping voltammetry in orange juice and helopyrin, a phytopharmaceutical preparation, *Electroanalysis*, 7, 1075, 1995.
17. Carrai, P., Nucci, L., and Pergala, F., Polarographic behavior of alachlor application to analytical determination, *Anal. Lett.*, 25, 163, 1992.
18. Babkina, S.S. and Ulakhovich, N.A., Amperometric biosensor based on denatured DNA for the study of heavy metals complexing with DNA and their determination in biological, water and food samples, *Bioelectrochemistry*, 63, 261, 2004.
19. Lo Coco, F. et al., Determination of lead (II) and cadmium (II) in hard and soft wheat by derivative potentiometric stripping analysis, *Anal. Chim. Acta*, 409, 93, 2000.
20. Luque, M. et al., Supported liquid membranes for the determination of vanillin in food samples with amperometric detection, *Anal. Chim. Acta*, 410, 127, 2000.
21. Desimoni, E., Brunetti, B., and Cosio, M.S., Determination of patent blue V (E131) at a Nafion-modified glassy carbon electrode, *Electroanalysis*, 18, 231, 2006.
22. Jayasri, D. and Narayanan, S.S., Manganese(II) hexacyanoferrate based renewable amperometric sensor for the determination of butylated hydroxyanisole in food products, *Food Chem.*, 101, 607, 2007.
23. Li, Y.H. et al., Determination of trace tin by anodic stripping voltammetry at a carbon paste electrode, *Electroanalysis*, 18, 976, 2006.
24. Miserere, S. et al., Biocompatible carbon-based screen-printed electrodes for the electrochemical detection of nitric oxide, *Electrochem. Commun.*, 8, 238, 2006.
25. Bouamrane, F. et al., Electrochemical study of diamond thin films in neutral and basic solutions of nitrate, *J. Electroanal. Chem.*, 405, 95, 1996.
26. Wang, J. et al., Bismuth-coated carbon electrodes for anodic stripping voltammetry, *Anal. Chem.*, 72, 3218, 2000.
27. De Souza, D., Machado, S.A.S., and Pires, R.C., Multiple square wave voltammetry for analytical determination of paraquat in natural water, food, and beverages using microelectrodes, *Talanta*, 69, 1200, 2006.
28. Radke, S.A. and Alocilja, E.C., A high density microelectrode array biosensor for detection of E-coli O157: H7, *Biosens. Bioelectron.*, 20, 1662, 2005.
29. Sánchez Arribas, A. et al., Voltammetric detection of the herbicide metatriton at a bismuth film electrode in nondeaerated solution, *Electroanalysis*, in press. AQ15
30. Schulze, H. et al., Development, validation, and application of an acetylcholinesterase-biosensor test for the direct detection of insecticide residues in infant food, *Biosens. Bioelectron.*, 17, 1095, 2002.
31. Adanyi, N. et al., Development of new immunosensors for determination of contaminants in food, *Curr. App. Phys.*, 6, 279, 2006.
32. Heinze, J., Cyclic voltammetry—"Electrochemical Spectroscopy," *Angew. Chem.*, 23, 831, 1984.
33. Kounaves, S.P., Voltammetric techniques, in *Handbook of Instrumental Techniques for Analytical Chemistry*, Settle, F. (Ed.), Prentice Hall PTR, 1997, chap. 37.
34. Stojek, Z., Pulse voltammetry, in *Electroanalytical Methods*, Scholz, F. (Ed.), Springer, Berlin/Heidelberg/New York, 2001, chap. II.
35. Lovric, M., Square-wave voltammetry, in *Electroanalytical Methods*, Scholz, F. (Ed.), Springer, Berlin/Heidelberg/New York, 2001, chap. II.
36. Osteryoung, J.G. and O'Dea, J.J., Square-wave voltammetry, in *Electroanalytical Chemistry*, Bard, A.J. (Ed.), Vol. 14, Marcel Dekker, New York, 1986.

37. Xu, G. et al., Adsorptive square-wave stripping voltammetry for determination of azobenzene at trace levels, *Anal. Chem.*, 66, 808, 1994.
38. Mirceski, V. et al., Square-wave voltammetry of 5-fluorouracil, *J. Electroanal. Chem.*, 490, 37, 2000.
39. Kalvoda, R. and Kopanica, M., Adsorptive stripping voltammetry in trace analysis, *Pure Appl. Chem.*, 61, 97, 1989.
40. Kounaves, S.P. et al., Square-wave anodic-stripping voltammetry at the mercury film electrode-theoretical treatment, *Anal. Chem.*, 59, 386, 1987.
41. Gulaboski, R. et al., Square-wave voltammetry of cathodic stripping reactions-diagnostic criteria, redox kinetic measurements, and analytical applications, *Electroanalysis*, 16, 832, 2004.
42. Lovric, M., Stripping voltammetry, in *Electroanalytical Methods*, Scholz, F. (Ed.), Springer, Berlin/Heidelberg/New York, 2001, chap. II.
43. Brainina, K. and Neyman, E., *Electroanalytical Stripping Methods*, Wiley-VCH, 1994.
44. Palleschi, G., Electrochemical biosensors for food analysis and the food industry, *Ital. J. Food Sci.*, 13, 137, 2001.
45. Mello, L.D. and Kubota, L.T., Review of the use of biosensors as analytical tools in the food and drink industries, *Food Chem.*, 77, 237, 2002.
46. Terry, L.A., White, S.F., and Tigwell, L.J., The application of biosensors to fresh produce and the wider Food industry, *J. Agric. Food Chem.*, 53, 1309, 2005.
47. Cavicchioli, A., La-Scalea, M.A., and Gutz, I.G.R., Analysis and speciation of traces of arsenic in environmental, food and industrial samples by voltammetry: A review, *Electroanalysis*, 16, 698, 2004.
48. Florence, T.M., Polarography of azo compounds and their metal complexes, *J. Electroanal. Chem. Interfacial Electrochem.*, 52, 115, 1974.
49. Fogg, A.G. and Yoo, K.S., Direct differential-pulse polarographic determination of mixtures of the food colouring matters tartrazine-Sunset Yellow FCF, tartrazine-Green S and amaranth-Green S in soft drinks, *Analyst*, 104, 723, 1979.
50. Ni, Y., Bai, J., and Jin, L., Simultaneous adsorptive voltammetric analysis of mixed colorants by multivariate calibration approach, *Anal. Chim. Acta*, 329, 65, 1996.
51. Kapor, M.A. et al., Electroanalysis of food dyes: Determination of indigo-carmin and tartrazine, *Eletica Quim.*, 26, 53, 2001.
52. Chanlon, S. et al., Determination of carmoisine, allura red and ponceau 4R in sweets and soft drinks by differential pulse polarography, *J. Food Composition Anal.*, 18, 503, 2005.
53. Berzas Nevado, J.J., Rodríguez Flores, J., and Villasenor Llerena, M.J., Adsorptive stripping voltammetry (ASV) of tartrazine at the hanging mercury drop electrode in soft drinks, *Fresenius J. Anal. Chem.*, 357, 989, 1997.
54. Combeau, S., Chatelut, M., and Vittori, O., Identification and simultaneous determination of Azorubin, Allura red and Ponceau 4R by differential pulse polarography: Application to soft drinks, *Talanta*, 56, 115, 2002.
55. Becerro Dominguez, F., Gonzalez Diego, F., and Hernandez Mendez, J., Determination of sunset yellow and tartrazine by differential pulse polarography, *Talanta*, 37, 655, 1990.
56. Berzas Nevado, J.J., Rodríguez Flores, J., and Villaseñor Llerena, M.J., Square wave adsorptive voltammetric determination of sunset yellow, *Talanta*, 44, 467, 1997.
57. Florian, M. et al., Determination of brilliant blue FCF in the presence and absence of erythrosine and quinoline yellow food colours by cathodic stripping voltammetry, *Food Additives Contaminants*, 19, 803, 2002.
58. Commission Regulation (EC) No 466/2001, *Off. J. Eur. Communities*, L 77/1, 8 March, 2001.
59. Kopanica, M. and Novotný, L., Determination of traces of arsenic(III) by anodic stripping voltammetry in solutions, natural waters and biological material, *Anal. Chim. Acta*, 368, 211, 1998.
60. Bryce, D.W., Izquierdo, A., and Luque de Castro, M.D., Flow-injection anodic stripping voltammetry at a gold electrode for selenium(IV) determination, *Anal. Chim. Acta*, 308, 96, 1995.
61. Zakharova, E.A., Pichugina, V.M., and Tolmacheva, T.P., Determination of mercury in water and alcoholic drinks by stripping voltammetry, *Zh. Anal. Khim.*, 51, 918, 1996.
62. Meryan, V.M., Chugureanu, D.G., and Zayats, G.D., Determination of cadmium in the presence of the 2,2'-dipyridyl-4,4-dihydroxybenzoic acid molecular complex and SCN^- ions by adsorption stripping voltammetry, *Zh. Anal. Khim.*, 53, 48, 1998.

63. Safavi, A. and Shams, E., Determination of trace amounts of copper(II) by adsorptive stripping voltammetry of its complex with pyrogallol red, *Anal. Chim. Acta*, 385, 265, 1999.
64. Meryan, V.T., Mokanu, R., and Taragan, N.F., Determination of nickel in the presence of eriochrome black T by adsorption stripping voltammetry, *Zh. Anal. Khim.*, 52, 463, 1997.
65. Gutierrez, C.A., Suarez, M.F., and Compton, R.G., Optimization of mercury thin film electrodes for sono-ASV studies, *Electroanalysis*, 11, 16, 1999.
66. Ji, Z. and Guadalupe, A.R., Reusable doped sol-gel graphite electrodes for metal ions determination, *Electroanalysis*, 11, 167, 1999.
67. Fomintseva, E.E., Zakharova, E.A., and Pikula, N.P., Determination of tin and lead in canned juices and fruit by stripping voltammetry, *Zh. Anal. Khim.*, 52, 590, 1997.
68. Adeloji, S.B.O. and Pablo, F., Adsorptive stripping voltammetric determination of ultratrace concentrations of molybdenum in biological and environmental materials on a glassy carbon mercury film electrode, *Electroanalysis*, 7, 476, 1995.
69. Abo-Maali, N. and Abd El-Hady, D., Square-wave stripping voltammetry of uranium(VI) at the glassy carbon electrode. Application to some industrial samples, *Electroanalysis*, 11, 201, 1999.
70. Faller, C. et al., Modified solid electrodes for stripping voltammetric determination of tin, *Fresenius J. Anal. Chem.*, 358, 670, 1997.
71. Matysik, F.-M., Gläser, P., and Werner, G., Analytical possibilities of microelectrode use for stripping voltammetry, *Fresenius J. Anal. Chem.*, 349, 646, 1994.
72. Wahdat, F., Hinkel, S., and Neeb, R., Direct inverse voltammetric determination of Pb, Cu and Cd in some edible oils after solubilisation, *Fresenius J. Anal. Chem.*, 352, 393, 1995.
73. Agra-Gutiérrez, C. et al., Anodic stripping voltammetry of copper at insonated glassy carbon-based electrodes: Application to the determination of copper in beer, *Analyst*, 124, 1053, 1999.
74. Babkina, S.S. and Ulakhovich, N.A., Amperometric biosensor based on denatured DNA for the study of heavy metals complexing with DNA and their determination in biological, water and food samples, *Bioelectrochemistry*, 63, 261, 2004.
75. Baldo, M.A., Bragato, C., and Daniele, S., Determination of lead and copper in wine by anodic stripping voltammetry with mercury microelectrodes: Assessment of the influence of sample pretreatment procedures, *Analyst*, 122, 1, 1997.
76. Kowalska, J. et al., Voltammetric determination of arsenic in plant material, *Electroanalysis*, 11, 1301, 1999.
77. Kowalska, J. and Golimowski, J., Voltammetric determination of arsenic in zinc oxide used as a feed additive, *Electroanalysis*, 10, 857, 1998.
78. Sancho, D. et al., Determination of copper and arsenic in refined beet sugar by stripping voltammetry without sample pretreatment, *Analyst*, 123, 743, 1998.
79. Aprea, C. et al., Biological monitoring of pesticide exposure: A review of analytical methods, *J. Chromatogr.*, 769, 191, 2002.
80. Garrido, E.M. et al., Electrochemical methods in pesticide control, *Anal. Lett.*, 37, 1755, 2004.
81. Terry, L.A., White, S.F., and Tigwell, L.J., The application of biosensors to fresh produce and the wider food industry, *J. Agric. Food. Chem.*, 53, 1309, 2005.
82. Hance, R.J., Polarography of herbicides—A preliminary survey, *Pest. Sci.*, 1, 112, 1970.
83. Ignjatovic, L.M. et al., Polarographic behavior and determination of some *s*-triazine herbicides, *Electroanalysis*, 5, 529, 1993.
84. Hernández Méndez, J., Carabias Martínez, R., and Rodríguez Gonzalo, E., Electroanalytical study of the pesticide guthion, *J. Electroanal. Chem.*, 244, 221, 1988.
85. Olmedo, C. et al., Polarographic study of the herbicide metatitron, *Electroanalysis*, 6, 694, 1994.
86. Pedrero, M. et al., Determination of the herbicide desmetryne in organised media by adsorptive stripping voltammetry, *Talanta*, 53, 991, 2001.
87. Yulaev, M.F. et al., Development of a potentiometric immunosensor for herbicide simazine and its application for food testing, *Sensors Actuators B*, 75, 129, 2001.
88. Subbalakshamma, M. and Reddy, S.J., Electrochemical reduction behavior and analysis of some organophosphorous pesticides, *Electroanalysis*, 6, 521, 1994.
89. De Souza, D. and Machado, S.A.S., Electroanalytical method for determination of the pesticide dichlorvos using gold-disk microelectrodes, *Anal. Bioanal. Chem.*, 382, 1720, 2005.
90. Sreedhar, N.Y. et al., Differential pulse polarographic determination of dicotophos, crotoxyphos and chlorfenvinphos in grains and soils, *Talanta*, 44, 1859, 1997.

91. Calvo-Marzal, P. et al., Electroanalytical determination of acid phosphatase activity by monitoring *p*-nitrophenol, *Anal. Chim. Acta*, 441, 207, 2001.
92. Southwick, L.M. et al., The polarographic reduction of some dinitroaniline herbicides, *Anal. Chim. Acta*, 82, 29, 1976.
93. Pedrero, M. et al., Determination of dinoseb by adsorptive stripping voltammetry using a mercury film electrode, *Fresenius J. Anal. Chem.*, 349, 546, 1994.
94. Del Carlo, M. et al., Screening of food samples for carbamate and organophosphate pesticides using an electrochemical bioassay, *Food Chem.*, 84, 651, 2004.
95. Aguí, L. et al., Determination of disulfiram by adsorptive stripping voltammetry at gold disk microelectrodes, *Electroanalysis*, 14, 486, 2002.
96. Bird, C.L. and Kuhn, A.T., Electrochemistry of the viologens, *Chem. Soc. Rev.*, 10, 49, 1981.
97. De Souza, D. and Machado, S.A.S., Electrochemical detection of the herbicide paraquat in natural water and citric fruit juices using microelectrodes, *Anal. Chim. Acta*, 546, 85, 2005.
98. Reviejo, A.J. et al., Determination of organochlorine pesticides in apple samples by differential-pulse polarography in emulsified medium, *Anal. Chim. Acta*, 264, 141, 1992.
99. Samatha, K. and Sreedhar, N.Y., Polarographic determination of deltamethrin, *Talanta*, 49, 53, 1999.
100. Zhang, Y. et al., Disposable biosensor test for organophosphate and carbamate insecticides in milk, *J. Agric. Food Chem.*, 53, 5110, 2005.
101. Albareda-Sirvent, M., Merkoçi, A., and Alegret, S., Pesticide determination in tap water and juice samples using disposable amperometric biosensors made using thick-film technology, *Anal. Chim. Acta*, 442, 35, 2001.
102. Olek, M., Blanchard, F., and Sudraud, G., Application de la détection électrochimique au dosage des résidus de quelques insecticides carbamates par chromatographie liquide haute performance, *J. Chromatogr. A*, 325, 239, 1985.
103. Nunes, G.S. et al., Determination of carbamate residues in crop samples by cholinesterase-based biosensors and chromatographic techniques, *Anal. Chim. Acta*, 362, 59, 1998.
104. Nunes, G.S. et al., Evaluation of a highly sensitive amperometric biosensor with low cholinesterase charge immobilized on a chemically modified carbon paste electrode for trace determination of carbamates in fruit, vegetable and water samples, *Anal. Chim. Acta*, 399, 37, 1999.
105. La Rosa, C. et al., Amperometric flow through biosensor for the determination of pesticides, *Anal. Chim. Acta*, 308, 129, 1995.
106. Nikolelis, D.P. et al., Flow injection analysis of carbofuran in foods using air stable lipid film based acetylcholinesterase biosensor, *Anal. Chim. Acta*, 537, 169, 2005.
107. Fernández, C., Reviejo, A.J., and Pingarrón, J.M., Development of graphite-poly(tetrafluoroethylene) composite electrodes voltammetric determination of the herbicides thiram and disulfiram, *Anal. Chim. Acta*, 305, 192, 1995.
108. Ivanov, A. et al., Cholinesterase sensors based on screen-printed electrodes for detection of organophosphorus and carbamic pesticides, *Anal. Bioanal. Chem.*, 377, 624, 2003.
109. Longobardi, F. et al., Use of electrochemical biosensor and gas chromatography for determination of dichlorvos in wheat, *J. Agric. Food Chem.*, 53, 9389, 2005.
110. del Carlo, M. et al., An electrochemical bioassay for dichlorvos analysis in durum wheat samples, *J. Food Prot.*, 69, 1406, 2006.
111. Concialini, V., Lippolis, M.T., and Galletti, G.C., Preliminary studies for the differential-pulse polarographic determination of a new class of herbicides: Sulphonylureas, *Analyst*, 114, 1617, 1989.
112. Palchetti, I. et al., Determination of anticholinesterase pesticides in real samples using a disposable biosensor, *Anal. Chim. Acta*, 337, 315, 1997.
113. Wagner, G. and Guibaud, G.G. (Ed.), *Food Biosensor Analysis*, Marcel-Dekker, New York, 1994.
114. Scott, A.O., *Biosensors for Food Analysis*, Royal Society of Chemistry, Cambridge, United Kingdom, 1998.
115. Del Carlo, M. et al., Biosensors for food quality assessment, in *Food Biotechnology*, Shetty, K., Paliyath, G., Pometto, A., and Levin, R. (Eds.), 2nd ed., CRC Press, Taylor & Francis Group, 2006.
116. Terry, L.A., White, S.F., and Tigwell, L.J., The application of biosensors to fresh produce and the wider food industry, *J. Agric. Food Chem.*, 53, 1309, 2005.
117. Palleschi, G. and Cubadda, R., Electrochemical biosensors for food analysis and the food industry, *Ital. J. Food Sci.*, 13, 137, 2001.

118. Dinçkaya, E. et al., Sulfite determination using sulfite oxidase biosensor based glassy carbon electrode coated with thin mercury film, *Food Chem.*, 101, 1540, 2007.
119. Kelly, S.C. et al., Development of an interferent free amperometric biosensor for determination of L-lysine in food, *Anal. Chim. Acta*, 412, 111, 2000.
120. Stobiecka, A., Radecka, H., and Radecki, J., Novel voltammetric biosensor for determining acrylamide in food samples, *Biosens. Bioelectron.*, in press.
121. Maestre, E., Katakis, I., and Dominguez, E., Amperometric flow-injection determination of sucrose with a mediated tri-enzyme electrode based on sucrose phosphorylase and electrocatalytic oxidation of NADH, *Biosens. Bioelectron.*, 16, 61, 2001.
122. Ferreira, V.S., Zanon, M.V.B., and Fogg, A.G., Indirect cathodic stripping voltammetric determination of ceftazidime as a mercury salt, *Anal. Chim. Acta*, 367, 255, 1998.
123. Portela, M.J. et al., Voltammetric method for the determination of the flavor enhancer inosinic acid, *Analyst*, 119, 2183, 1994.
124. Rodrigues, P.G. et al., Automatic flow system with voltammetric detection for diacetyl monitoring during brewing process, *J. Agric. Food Chem.*, 50, 3647, 2002.
125. Rodrigues, J.A., Barros, A.A., and Rodrigues, P.G., Differential pulse polarographic determination of -dicarbonyl compounds in foodstuffs after derivatization with o-phenylenediamine, *J. Agric. Food Chem.*, 47, 3219, 1999.
126. Michelitsch, A. and Wurglics, M., Electrochemical oxidation of hyperforin on glassy carbon electrode and determination in herbal medicinal products, *Electroanalysis*, 15, 797, 2003.
127. Kaláb, T. and Skládal, P., Evaluation of different mediators for the development of amperometric microbial bioelectrodes, *Electroanalysis*, 6, 1004, 1994.
128. Xu, Y.F., Velasco-Garcia, M., and Mottram, T.T., Quantitative analysis of the response of an electrochemical biosensor for progesterone in milk, *Biosens. Bioelectron.*, 20, 2061, 2005.
129. Laschi, S. et al., Polychlorinated biphenyls (PCBs) detection in food samples using an electrochemical immunosensor, *J. Agric. Food Chem.*, 51, 1816, 2003.
130. Lin, L.A., Detection of alkaloids in foods with a multi-detector high-performance liquid chromatographic system, *J. Chromatogr. A*, 632, 69, 1993.
131. Yu, H., Ding, Y.S., and Mou, S.F., Direct and simultaneous determination of amino acids and sugars in rice wine by high-performance anion-exchange chromatography with integrated pulsed amperometric detection, *Chromatographia*, 57, 721, 2003.
132. Van Dyck, M.M.C., Rollmann, B., and De Meester, C., Quantitative estimation of heterocyclic aromatic amines by ion-exchange chromatography and electrochemical detection, *J. Chromatogr. A*, 697, 377, 1995.
133. Siu, D.C. and Henshall, A., Ion chromatographic determination of nitrate and nitrite in meat products, *J. Chromatogr. A*, 804, 157, 1998.
134. Xu, J.M. et al., Determination of electroinactive organic acids in red wine by ion-exclusion chromatography using a poly-o-phenylenediamine film modified electrode, *Chromatographia*, 57, 751, 2003.
135. Klejdus, B. et al., Determination of isoflavones in soybean food and human urine using liquid chromatography with electrochemical detection, *J. Chromatogr. B*, 806, 101, 2004.
136. Schneiderman, M.A., Sharma, A.K., and Locke, D.C., Determination of vitamin A palmitate in cereal products using supercritical fluid extraction and liquid chromatography with electrochemical detection, *J. Chromatogr. A*, 765, 215, 1997.
137. Galceran, M.T., Pais, P., and Puignou, L., High-performance liquid chromatographic determination of ten heterocyclic aromatic amines with electrochemical detection, *J. Chromatogr. A*, 655, 101, 1993.
138. Rivera, L. et al., Solid-phase extraction for the selective isolation of polycyclic aromatic hydrocarbons, azaarenes and heterocyclic aromatic amines in charcoal-grilled meat, *J. Chromatogr. A*, 731, 85, 1996.
139. Galeano Díaz, T. et al., Determination of nitrofurantoin, furazolidone and furaltadone in milk by high-performance liquid chromatography with electrochemical detection, *J. Chromatogr. A*, 764, 243, 1997.
140. Iwase, H., Use of an amino acid in the mobile phase for the determination of ascorbic acid in food by high-performance liquid chromatography with electrochemical detection, *J. Chromatogr. A*, 881, 317, 2000.
141. Schultheiss, J., Jensen, D., and Galensa, R., Determination of aldehydes in food by high-performance liquid chromatography with biosensor coupling and micromembrane suppressors, *J. Chromatogr. A*, 880, 233, 2000.

AQ16

AQ17

142. Lookabaugh, M. and Krull, I.S., Determination of nitrite and nitrate by reversed-phase high-performance liquid chromatography using on-line post-column photolysis with ultraviolet absorbance and electrochemical detection, *J. Chromatogr.*, 452, 295, 1988.
143. Mattila, P., Lehtonen, M., and Kumpulainen, J., Comparison of in-line connected diode array and electrochemical detectors in the high-performance liquid chromatographic analysis of coenzymes Q₉ and Q₁₀ in food materials, *J. Agric. Food Chem.*, 48, 1229, 2000.

AUTHOR QUERIES

- [AQ1] Please check the edited Running head.
- [AQ2] Please check and clarify if it is “3 to 1 kg” or “3 to 10 kg” in “Nowadays... ranges”.
- [AQ3] Please provide the expansion of “DME:” in “Mercury... film electrodes”, if appropriate.
- [AQ4] Shall we change “resulting simulated voltammogram” to “result-simulated voltammogram” in the figure captions?
- [AQ5] Shall we change “Such amalgamated... direction” to “After amalgamation... direct”?
- [AQ6] Please check “... and therefore the importance of established health and risk regulations” for sense.
- [AQ7] Please provide the expansion of “NGCE” and “ASSWV” in Table 17.2, if appropriate.
- [AQ8] Please check and clarify if the section number is correct in “The well-known... analysis (see Section 17.7.4)”.
- [AQ9] Please provide the expansion for the following abbreviations in Table 17.3, if appropriate: MWAAD, CAdSV, SSWASV, OSWV, LASSV, LSV, MTFE, SGE, GCE, CCE, SMFE, MF_μE.
- [AQ10] Should “Clorofenvinphos” be changed to “Chlorfenvinphos”?
- [AQ11] Please provide the expansion of “UME” in Table 17.4, if appropriate.
- [AQ12] Should “poisoning” be changed to “contaminant”?
- [AQ13] Please provide the place of publication in References 4, 12, 33, 43, 115.
- [AQ14] Please check if the chapter numbers are correct in References 10, 11, 34, 35, 42.
- [AQ15] Please update Reference 29.
- [AQ16] Please update Reference 120.
- [AQ17] Please check and clarify if the hyphen before “dicarbonyl” should be deleted or something is missing in Reference 125.